
Intramolecular alkylation of 3- and 4-halogenoalkyldiphenylphosphine sulfides. Ring-chain halogenotropic tautomerism of 2,2-diphenyl-1,2λ⁴-thiaphospholanium and 2,2-diphenyl-1,2λ⁴-thiaphosphorinanium iodides

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Heating of 3- and 4-chloroalkyldiphenylphosphine sulfides **1a,b** with sodium iodide in acetone leads to 2,2-diphenyl-1,2λ⁴-thiaphospholanium iodide **2a** and 2,2-diphenyl-1,2λ⁴-thiaphosphorinanium iodide **2b**; relatively uncommon ring-chain halogenotropic tautomerism is observed in solutions of these compounds.

Tertiary phosphine sulfides are known^{1,2} to react with alkyl halides to yield alkylthiophosphonium salts, reaction (1).



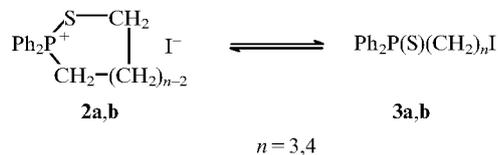
The phosphonium structure of the alkylation product obtained from trimethylphosphine sulfide and methyl iodide was confirmed by X-ray analysis.³ We have found that by refluxing 3- and 4-chloroalkyldiphenylphosphine sulfides **1a,b**⁴

protons of the $(\text{CH}_2)\text{CH}_2(\text{Hlg})$ group (*cf.* ref. 4). The tautomeric equilibrium (**2a,b** \rightleftharpoons **3a,b**) is established only slowly (within a few days at 20 °C). The equilibrium position depends on the solvent used and the ring size. According to the ^{31}P NMR spectra 30% of the open form **3a** is present in a CH_2Cl_2 solution of **2a** and 13% in CHCl_3 .

Table 1 ^{31}P NMR spectral data for **2** and **3** in various solvents (δ , ppm).

Solvent	2a	3a	2b	3b
CH_2Cl_2	72.2	41.4	37.6	42.2
CHCl_3	72.2	41.1	37.8	42.5
MeCN	73.3	—	38.1	—

At the same time the equilibrium is completely shifted to the ring form **2a** in MeCN; *i.e.* the content of the less polar ring-opened form **3a** in a tautomeric mixture decreases with increasing solvent polarity. The relative amounts of the open form **3** also decreases in the case of **2a** compared to **2b** which possesses a less strained six-membered $1,2\lambda^4$ -thiaphosphori-



§ For comparison: δ_{P} (CH_2Cl_2) for 3- and 4-chloroalkyldiphenylphosphine sulfides **1a,b** 41.2 and 42.7 ppm, respectively;⁴ δ_{P} for $\text{Ph}_2\text{P}(\text{S})\text{Bu}$ 42.8 ppm.⁹

nane ring. There is 15% of the open form **3b** in CH_2Cl_2 solution of **2b** and 8% in CHCl_3 . In MeCN solution, as in the case of **2a**, the equilibrium is completely shifted to the ring form **2b**.

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